Electronic Supplementary Material (ESI) for CrystEngComm.

Metal-organic Segments Induced Dimensionality Evolution in Polyoxometalate-based Hybrids

(Electronic Supplementary Information)

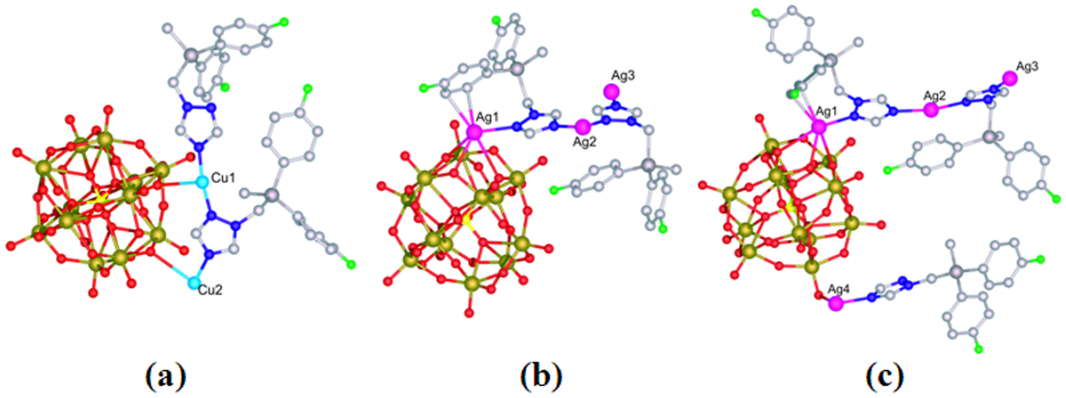

Figure S1. Asymmetric units of compounds **1** (a), **2** (b) and **3** (c), respectively.

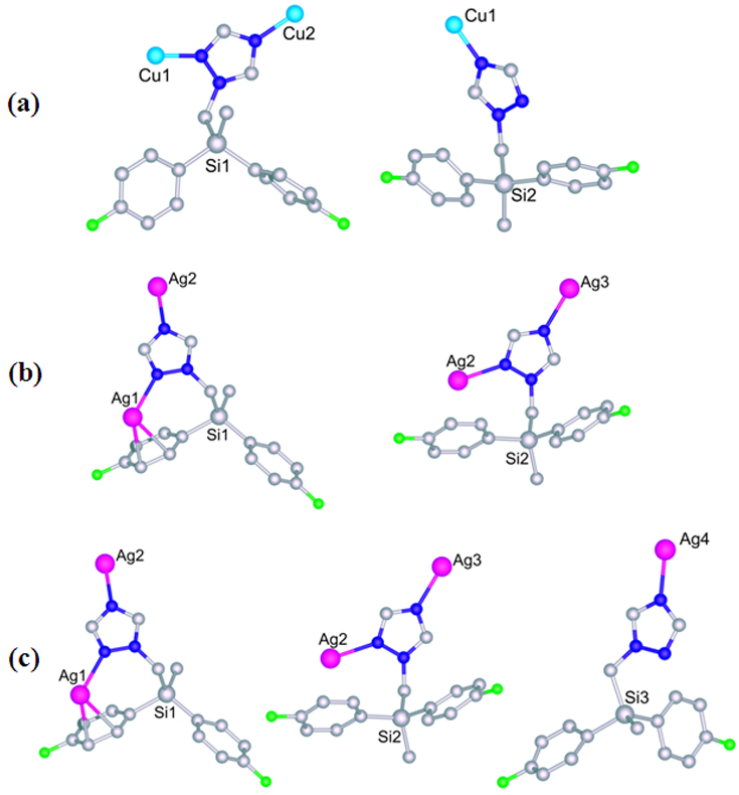

Figure S2. Coordination modes of fsa ligands in compounds **1**(a), **2** (b) and 3 (c), respectively.

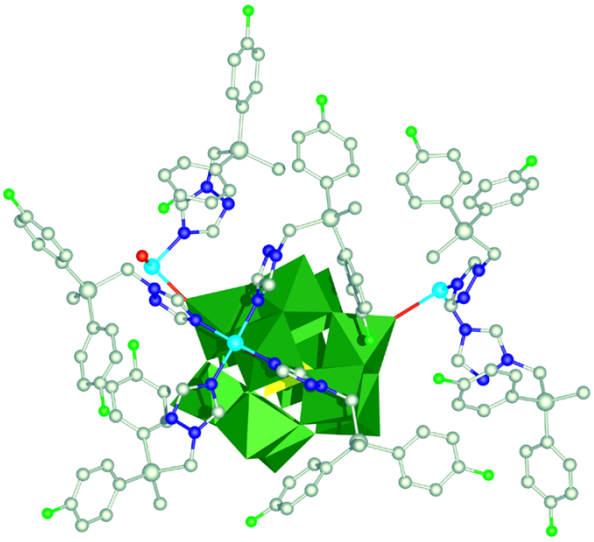

Figure S3. Asymmetric unit of compound **4**.

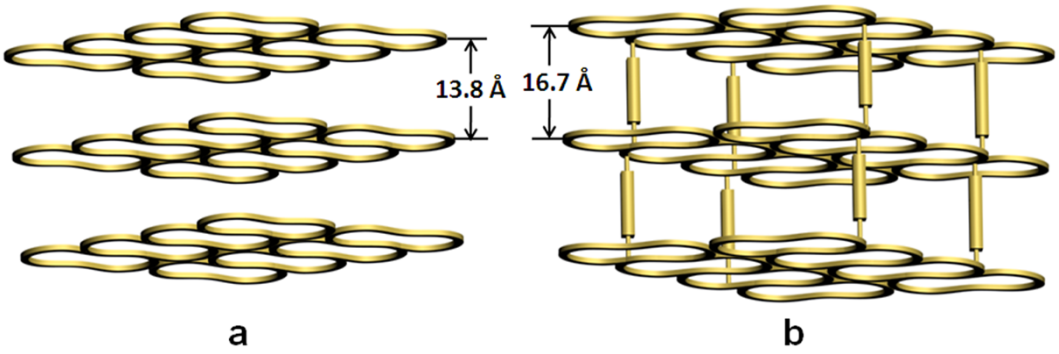

Figure S4. Schematic comparison of 3D frameworks between **2** (a) and **3** (b).

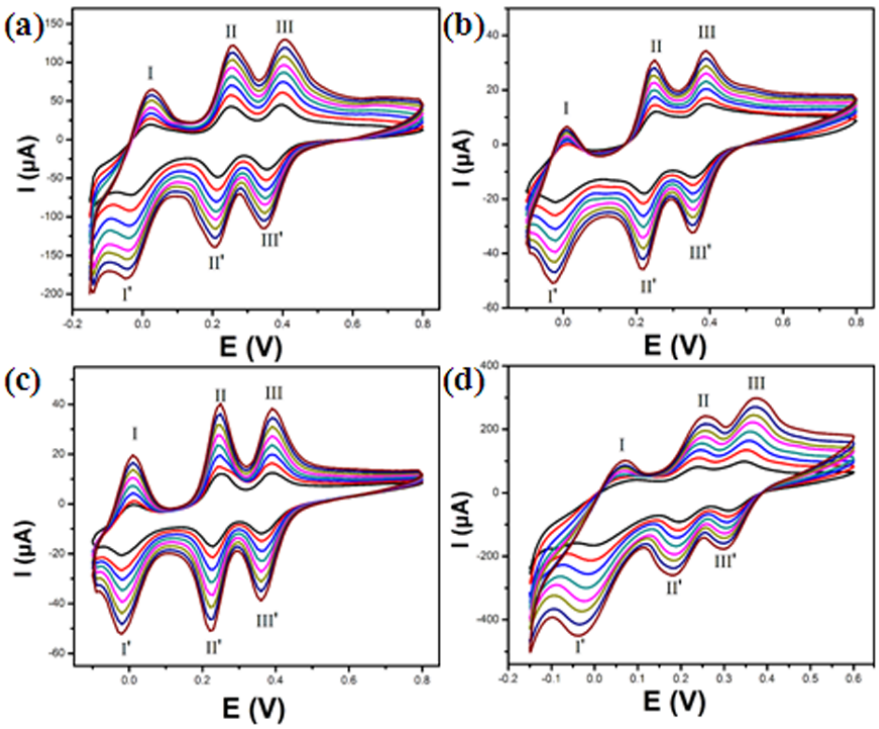

Figure S5. CV curves of 1-CPE (a), 2-CPE (b), 3-CPE (c) and 4-CPE (d) in 1 M H_2SO_4 at different scan rates (from inner to outer: 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4 and 0.45 V s^{-1}).

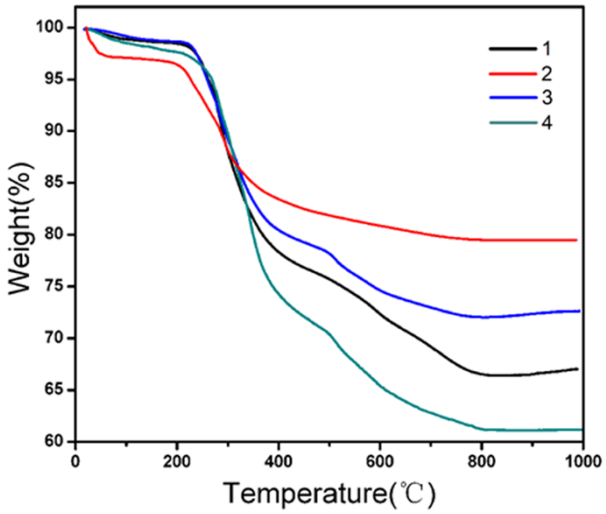

Figure S6. TG curves of compounds **1-4**. The TG experiments were performed under N_2 atmosphere with a heating rate of 10 ℃ min^{-1} in the temperature range of 30-1000 ℃. In the TG curves, the weight loss of 38.48% (calc. 38.53%) for compound **1**, 23.42% (calc. 23.17%) for **2**, 30.52% (calc. 30.60%) for **3**, and 24.12% (calc. 24.05%) for **4** from 200 to 800 ℃ correspond to the loss of fsa molecules.

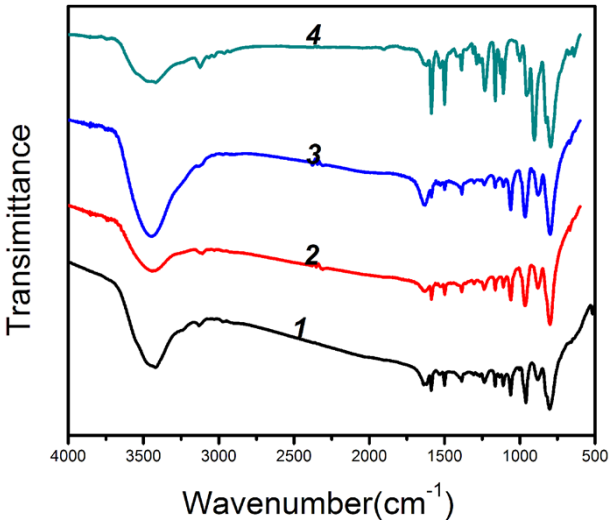

Figure S7. IR spectra of compounds **1**-**4**.

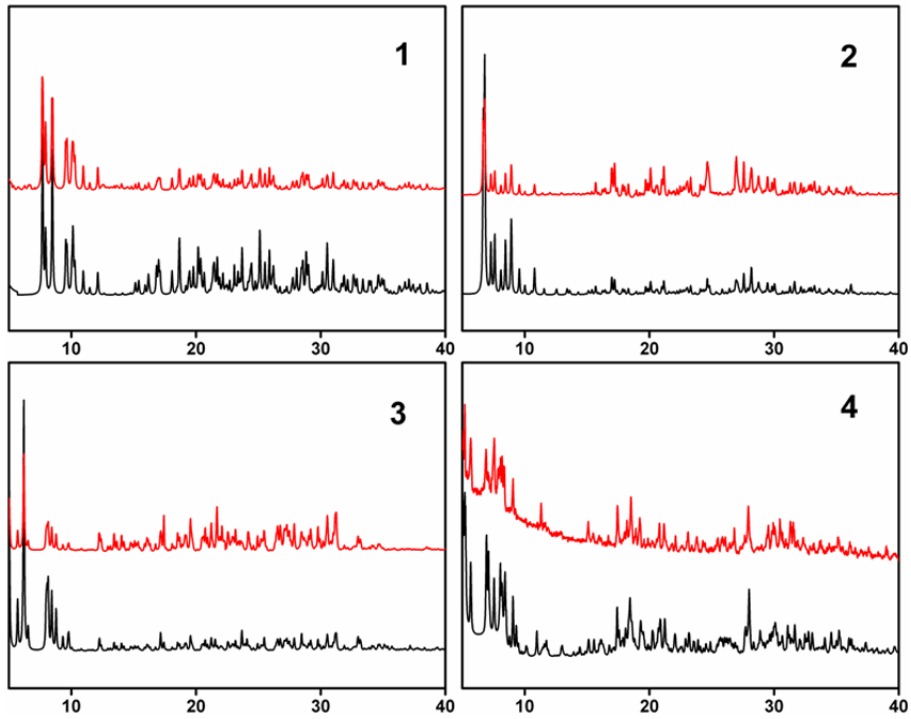

Figure S8. Powder XRD patterns for **1**-**4**: simulated (black) and experimental (red).

Table S1. Selected bond distances (Å) and angles (°) for **1**-**4**.

1			
Cu(1)-N(5)	1.874(4)	Cu(1)-N(1)	1.884(4)
Cu(1)-O(11)	2.668(1)	Cu(2)-N(2)	1.885(4)

Cu(2)-N(2)#2	1.885(4)		
N(5)-Cu(1)-N(1)	170.72(19)	N(2)-Cu(2)-N(2)#2	180.00(17)
O(11)-Cu(1)-N(5)	96.501(17)	O(11)-Cu(1)-N(1)	90.325(15)
2			
Ag(1)-N(1)	2.275(9)	Ag(1)-O(12)	2.397(9)
Ag(1)-C(5)	2.472(15)	Ag(1)-C(6)	2.497(13)
Ag(2)-N(2)	2.143(10)	Ag(2)-N(4)	2.147(11)
Ag(3)-N(5)	2.125(18)	Ag(3)-N(5)#1	2.132 (18)
N(1)-Ag(1)-O12(1)	123.2(3)	N(1)-Ag(1)-C(5)	100.6(4)
O(12)-Ag(1)-C(5)	132.3(4)	N(1)-Ag(1)-C(6)	126.1(4)
O(12)-Ag(1)-C(6)	110.7(4)	C(5)-Ag(1)-C(6)	31.5(4)
N(2)-Ag(2)-N(4)	162.1(5)	N(5)-Ag(3)-N(5)#1	165.2(4)
3			
Ag(1)-N(1)	2.287(4)	Ag(1)-O(18)	2.418(4)
Ag(1)-C(8)	2.572(6)	Ag(1)-C(9)	2.595(6)
Ag(2)-N(2)	2.146(4)	Ag(2)-N(4)	2.168(4)
Ag(3)-N(5)	2.138(4)	Ag(3)-N(5)#1	2.138(4)
Ag(4)-N(8)#2	2.118(5)	Ag(4)-N(8)	2.118(5)
O(18)-Ag(1)-C(8)	117.39(16)	O(18)-Ag(1)-C(9)	142.13(16)
N(1)-Ag(1)-O(18)	122.25(14)	N(1)-Ag(1)-C(8)	119.35(18)
N(1)-Ag(1)-C(9)	94.66(17)	C(8)-Ag(1)-C(9)	31.48(19)
N(2)-Ag(2)-N(4)	164.35(18)	N(5)-Ag(3)-N(5)#1	180.0(3)
N(8)-Ag(4)-N(8)#2	180.00(19)		
4			
Cu(1)-N(4)	2.016(11)	Cu(1)-N(7)	2.012(12)
Cu(1)-N(1)	2.023(11)	Cu(1)-N(10)	2.033(12)
Cu(1)-O(24)	2.306(8)	Cu(2)-N(13)#1	1.980(13)
Cu(2)-N(13)	1.980(13)	Cu(2)-N(16)#1	2.054(12)
Cu(2)-N(16)	2.054(12)	Cu(2)-O(33)	2.404(9)

Cu(2)-O(33)#1	2.404(9)	Cu(3)-N(19)#2	1.969(12)
Cu(3)-N(19)	1.969(12)	Cu(3)-O(11)#2	2.003(9)
Cu(3)-O(11)	2.003(9)	Cu(3)-O(1W)	2.387(10)
Cu(3)-O(1W)#2	2.387(10)		
N(4)-Cu(1)-N(7)	91.9(5)	N(4)-Cu(1)-N(1)	175.4(4)
N(7)-Cu(1)-N(1)	90.0(5)	N(4)-Cu(1)-N(10)	90.4(5)
N(7)-Cu(1)-N(10)	177.6(5)	N(1)-Cu(1)-N(10)	87.6(5)
N(4)-Cu(1)-O(24)	87.3(4)	N(7)-Cu(1)-O(24)	90.5(4)
N(1)-Cu(1)-O(24)	96.9(4)	N(10)-Cu(1)-O(24)	90.3(4)
N(13)#1-Cu(2)-N(13)	180.0(6)	N(13)#1-Cu(2)-N(16)#1	88.2(5)
N(13)-Cu(2)-N(16)#1	91.8(5)	N(13)#1-Cu(2)-N(16)	91.8(5)
N(13)-Cu(2)-N(16)	88.2(5)	N(16)#1-Cu(2)-N(16)	180.0(6)
N(13)#1-Cu(2)-O(33)	87.8(4)	N(13)-Cu(2)-O(33)	92.2(4)
N(16)#1-Cu(2)-O(33)	95.1(4)	N(16)-Cu(2)-O(33)	84.9(4)
N(13)#1-Cu(2)-O(33)#1	92.2(4)	N(13)-Cu(2)-O(33)#1	87.8(4)
N(16)#1-Cu(2)-O(33)#1	84.9(4)	N(16)-Cu(2)-O(33)#1	95.1(4)
O(33)-Cu(2)-O(33)#1	180.0(5)	N(19)#2-Cu(3)-N(19)	180.000(2)
N(19)#2-Cu(3)-O(11)#2	91.4(4)	N(19)-Cu(3)-O(11)#2	88.6(4)
N(19)#2-Cu(3)-O(11)	88.6(4)	N(19)-Cu(3)-O(11)	91.4(4)
O(11)#2-Cu(3)-O(11)	180.0(5)	N(19)#2-Cu(3)-O(1W)	89.0(4)
N(19)-Cu(3)-O(1W)	91.0(4)	O(11)#2-Cu(3)-O(1W)	89.2(4)
O(11)-Cu(3)-O(1W)	90.8(4)	N(19)#2-Cu(3)-O(1W)#2	91.0(4)
N(19)-Cu(3)-O(1W)#2	89.0(4)	O(11)#2-Cu(3)-O(1W)#2	90.8(4)
O(11)-Cu(3)-O(1W)#2	89.2(4)	O(1W)-Cu(3)-O(1W)#2	180.000(2)

Symmetry code: for **1**: #1 -x+1, -y+1, -z; #2 -x, -y+2, -z; for **2**: #1 -x+1, -y, -z; #2 -x, -y, -z; for **3**: #1 1-x, -y, 1-z; #2 1-x, 2-y, -z; for **4**: #1 -x, -y+1, -z+1; #2 -x+1, -y+1, -z+1.